

EUROPEAN PATENT OFFICE

Patent Abstracts of Japan

cited in the European Search
Report of EP(0.11.18195)
Your Ref.: FK-200(PH-1596807)

PUBLICATION NUMBER : 01132858
PUBLICATION DATE : 25-05-89

APPLICATION DATE : 24-05-88
APPLICATION NUMBER : 63127677

APPLICANT : KURARAY CO LTD;

INVENTOR : YAMASHITA SADAO;

INT.CL. : D04H 1/42 D04H 1/72

TITLE : NONWOVEN FABRIC FROM POLYURETHANE EXTRA-FINE ELASTIC FIBER

ABSTRACT : PURPOSE: To obtain the subject nonwoven fabric that has excellent texture, flexibility, extensibility, moisture-permeating and waterproofing properties and high durability by melt-spinning a thermoplastic polyurethane prepared from a specific polyester diol, treating the melt-extruded polymer with high- temperature and high-speed gas into ultrafine fiber flow and collecting them in a sheet.

CONSTITUTION: 3-Methyl-1,5-pentanediol, or a mixed diol mainly comprising the same is reacted with dicarboxylic acids to form a polyester diol with an average molecular weight of 600-3,000. This polyester diol is reacted with a polyisocyanate to obtain a thermoplastic polyurethane. Then, the polyurethane is melt-extruded through the spinning nozzles, simultaneously a high-temperature and high-speed gas is injected from the nozzles attached to the adjacent position to make the polyurethane polymer into ultrafine fiber flows with an average fiber diameter of $\leq 12 \mu$ and they are collected in sheets that have excellent texture, flexibility, stretchability, moisture permeation and waterproofness.

COPYRIGHT: (C)1989,JPO

Japanese Patent Application Laid-Open No. Hei-01-132858

(43) Date of publication of application: 25.05.1989

(51) Int. Cl.: D04H 1/42

D04H 1/72

(21) Application number: 63-127677

(22) Date of filing: 24.05.1988

(30) Priority

Priority number: 62195527

Priority date: 04.08.1987

Priority country: JP

(72) Inventor: ASANO MASAJI

OKADA HIROMASA

YAMASHITA SADAOK

(71) Applicant: KURARAY CO., LTD

(54) Title of the Invention: NON-WOVEN FABRIC MADE FROM
POLYURETHANE ULTRA-FINE ELASTIC FIBER

SPECIFICATION

Title of the Invention

NON-WOVEN FABRIC MADE FROM POLYURETHANE
ULTRA-FINE ELASTIC FIBER

What is claimed is:

A non-woven fabric made from polyurethane ultra-fine elastic fiber produced by melt spinning a thermoplastic polyurethane from a spinning nozzle, simultaneously jetting high speed gas flow of an elevated temperature from a gas discharge nozzle disposed adjacent to the spinning nozzle, thereby collecting a flow of extra-thin elastic fibers, and collecting them to sheet form, wherein the thermoplastic polyurethane is formed by the use of a polyester diol with an averaged molecular weight of 600 to 3000 as a polymer diol obtained by the reaction of 3-methyl-1,5-pentanediol or a mixed diol mainly containing the 3-methyl-1,5-pentanediol with dicarboxylic acid,

and wherein the average diameter of the polyurethane ultra-fine elastic fiber is 12 μ m or smaller, and having sufficiently comfortable tactile, flexibility, elasticity and moisture permeable waterproof property, and at the same time, with supreme durability of these properties.

Detailed Description of the Invention

[Technical field of the invention]

The present invention relates to a non-woven fabric made from polyurethane ultra-fine elastic fiber.

[Prior art]

Various technologies are proposed regarding non-woven fabrics made from various kinds of polyurethane elastic fibers.

For example, Japanese Laid Open Patent Application No. Shou 52-31177 proposes non-woven fabrics made from dry processed polyurethane elastic fibers. However, the dry spinning process causes insufficient open fabric induced by strong adhesion between fabric with an ordinary fineness of themselves and the non-woven fabric made from dry processed polyurethane elastic fibers becomes these with hard textures thereby resulting in having the appearance and tactile of polyurethane film different from the appearance and tactile of the non-woven fabrics.

On the other hand, Japanese Laid Open Patent Application No. Shou 59-223347 proposes non-woven fabrics made from molten polyurethane elastic fibers. It is taught that the non-woven fabric is made by the melt spinning process comprising the steps of jetting gas flow of an elevated temperature after melt processing thermoplastic polyurethane, laminating the resultant filament after thinning without substantially bundling, and adhering the intersections of the laminated filaments with the filaments themselves. In this technology, the molten polyurethane elastic fibers form the non-woven fabric without adhesion accompanying the dry processed polyurethane elastic fibers and without substantially bundling. Accordingly, the resultant non-woven fabric achieves flexibility, elasticity and air-permeability.

[Problems to be solved by the invention]

However, it is difficult for the melt spinning process to stably and uniformly thin by jetting high-speed gas flow. Therefore, it is extremely difficult to obtain the non-woven fabric with little adhesion and without

substantially bundling of the fibers among themselves. In particular, it is almost impossible to substantially eliminate the bundling of the fibers among themselves.

Namely, the use of the polyurethane obtained by synthesizing polyether polyol as a soft segment component induces exaggerating heat decomposition at melt situation, and remarkably reduces elastic property of the polyurethane thereby loses practical elasticity of the non-woven fabric.

Further, although the use of the polyurethane obtained by synthesizing polyester polyol as a soft segment component improves the heat decomposition at melt situation as compared with the use of the polyurethane obtained by synthesizing polyether polyol as a soft segment component, it reduces degree of polymerization in melt spinning process when compared with the ordinary polymers. Therefore, the non-woven fabric made from ultra-fine elastic fiber was not practically usable because the durability, especially hydrolysis resistance, loses its intrinsic property.

The present invention was achieved by eagerly investigating the problems in the prior art.

It is an object of the present invention to provide a non-woven fabric made from polyurethane ultra-fine elastic fiber with sufficiently comfortable tactile, flexibility, elasticity and moisture permeable waterproof property, and at the same time, with supreme durability of these properties without substantially eliminating the bundling of the fibers among themselves.

[Means to solve the problem]

According to the present invention, the foregoing object is achieved by a non-woven fabric made from polyurethane ultra-fine elastic fiber produced by melt spinning a thermoplastic polyurethane from a spinning nozzle, simultaneously jetting high speed gas flow of an elevated temperature from a gas discharge nozzle disposed adjacent to the spinning nozzle, thereby generating a flow of ultra-fine elastic fibers, and collecting them to sheet form, wherein the thermoplastic polyurethane is formed by the use of a polyester diol with an average molecular weight of 500 to 3000 as a polymer diol obtained by the reaction of 3-methyl-1,5-pentanediol or a mixed glycol mainly containing the 3-methyl-1,5-pentanediol with dicarboxylic acid, and wherein the average diameter of the polyurethane ultra-fine elastic fiber is 7 μ m or smaller.

The thermoplastic polyurethane constituting the non-woven fabric

made from polyurethane ultra-fine elastic fiber according to the present invention is a thermoplastic polyurethane (hereunder, may be abbreviated as "TPU") obtained by the reaction of an polyester diol (hereunder, may be abbreviated as "MPD base PES diol") having hydroxy group at terminal end comprising 3-methyl-1,5-pentanediol or a mixed glycol mainly containing the 3-methyl-1,5-pentanediol and dicarboxylic acid with an organic diisocyanate.

In the foregoing description, typical examples of the glycol employed by mixing with 3-methyl-1,5-pentanediol include aliphatic diol having 2 to 10 carbon atoms such as ethylene glycol, butane diol, hexane diol, propylene glycol, neopentyl glycol and nonane diol, polyalkylene polyol such as diethylene glycol. The glycol may be used alone or in combination of two or more kinds thereof. The usage of many amount of the diol is unfavorable because it reduces the effects of the present invention. The usage of the diol in the process of preparing the MPD base PES diol is within 40 % by weight as against the glycol component, and is preferably within 20 % by weight there as.

Further, aliphatic dicarboxylic acid or aromatic carboxylic acid is favorably employed as the dicarboxylic acid. Typical examples include aliphatic dicarboxylic acid having 4 to 12 carbon atoms such as succinic acid, adipic acid, azelaic acid, and sebacic acid, or aromatic carboxylic acid having 4 to 12 carbon atoms such as isophthalic acid and terephthalic acid.

The foregoing polyester diol can be prepared by the same process as the well known process, in other words, an ester interchange or a direct esterification and subsequent melt polycondensation reaction. The averaged molecular weight of the polyester diol is desirably in the range of from 600 to 3000, and is preferably in the range of from 800 to 2000. Too small average molecular weight would degrade the elastic property at the timing of melt of the polyurethane obtained by reacting with the organic diisocyanate, and although the extra thinning by simultaneous melt spinning and ejection of high speed gas flow of the elevated temperature is easily conducted, the elastic property, i.e. elasticity, of the resultant non-woven fabric made from polyurethane extra-thin elastic fiber deteriorates and the heat resistance or the characteristics under low temperature thereof also extremely deteriorates. On the other hand, too large averaged molecular weight would make the extra thinning by simultaneous melt spinning and jetting of high speed gas flow of the elevated temperature extremely difficult and inhibit

the formation of ultra-fine polyurethane fiber flow. As a result, any non-woven fabric made from polyurethane elastic fiber with comfortable tactile and flexibility cannot be obtained. Appropriate examples of the organic diisocyanate employed for preparing the TPU include well known aliphatic, alicyclic or aromatic organic diisocyanate having 2 or more isocyanate group in the molecule, particularly diisocyanate such as 4,4'-diphenyl methane diisocyanate, p-phenylene diisocyanate, toluylenediisocyanate, 1,5-naphtylene diisocyanate, xylylene diisocyanate, hexamethylene diisocyanate, isoholone diisocyanate, 4,4'-dicyclohexyle diisocyanate etc. Among these, 4,4'-diphenyl methane diisocyanate is preferable in the viewpoint of the mechanical property of the TPU as the product.

Additionally, an appropriate chain elongation agent may be optionally used in the present invention. Examples of the chain elongation agent include conventionally used continuous chain growing agent for polyurethane, i.e. compound with low molecular weight of 400 or lower having at least two hydrogen atoms having reaction capability with isocyanate, such as ethylene glycol, propylene glycol, 1,4-butane diol, 1,6-hexane diol, 3-methyl-1,5-pentane diol, cyclohexane diol, xylylene glycol, 1,4-bis(β -hydroxyethoxy)benzene, neopentile glycol, 3,3'-dichloro-4,4'-diamynodiphenyl methane, isophorone diamine, 4,4'-diaminodiphenylemethane, hydrazine, dihydrazide trimethylolpropane and glycerin. Among these, 1,4-butane diol, 1,4-bis(β -hydroxyethoxy)benzene, 3-methyl-1,5-pentane diol, or their mixed compound may be most efficiently applicable. Depending on the situation, polymer diol such as polyethylene diol, poly tetramethylene diol, poly caprolactone diol or polymer diol such as poly caprolactone diol may be applicable as far as it does not lose the molding ability.

As the synthesizing method for polyurethane employed for the present invention, well-known method disclosed in, for example, Japanese Examined Patent Publication No. Shou 47-34494.

Subsequently, an important point of the present invention resides in melt spinning a thermoplastic polyurethane from a spinning nozzle, simultaneously ejecting high speed gas flow of an elevated temperature from the gas discharge nozzle deployed adjacent to the spinning nozzle, thereby generating a flow of ultra fine elastic fibers having average single diameter

of 12 μ m or smaller, and collecting them to sheet form.

Namely, an intension of producing a non-woven fabric from an ordinary melt spun polyurethane through spinning, winding, crimping and carding in accordance with a production process of cut-staple fails to obtain fine polyurethane fiber having average single diameter of 12 μ m or smaller by melt spinning. Further, the elastic property of the polyurethane fibers obstructs to endow crimping adaptive for carding and substantially makes the formation of non-woven fabric impossible. On the contrary, melt spinning the thermoplastic polyurethane from a spinning nozzle, simultaneously jetting high speed gas flow of an elevated temperature from the gas discharge nozzle makes it possible to obtain non-woven fabric wherein the average diameter of the single polyurethane ultra-fine elastic fiber is 12 μ m or smaller.

Still further, an extremely important point is that the average diameter of the polyurethane ultra-fine elastic fiber is 12 μ m or smaller:

In other words, although the problems of mutual bundling or adhesion of single fiber in the thinning process under jetting high speed gas flow of an elevated temperature are not overcome, the ultra-super-fine polyurethane fiber having average single diameter of 12 μ m or smaller accelerates the resultant non-woven fabric made from polyurethane ultra-fine elastic fiber to reveal a warm and comfortable tactile, flexibility, elasticity, moisture-permeability and waterproof property specialized in fabric cloth completely different from cold texture like polyurethane film.

The average diameter of the polyurethane ultra-fine elastic fiber is preferably 10 μ m or smaller. When the average diameter exceeds 12 μ m, the remained problems of mutual bundling or adhesion of single fiber in the thinning process gives cold texture like films, poor flexibility, coarse and hard tactile to the resultant non-woven fabric. Regarding the moisture-permeable and waterproof property, an extremely deteriorated waterproof property would deny the practical use.

The polyurethane ultra-fine elastic fiber of the present invention may be produced by an ordinary meltblown method.

Namely, with the use of the meltblown production apparatus disclosed in Japanese Laid Open Patent Application No. Shou 49-48921, melt-spinning thermoplastic polyurethane obtained by melting polymerization of polyester diol having mean molecular weight of 1000

comprising 3-methyl-1,5-pentanediol and adipic acid, 1,4-butane diol and 4,4-diphenyl methane diisocyanate from a spinning nozzle, simultaneously jetting high speed gas flow of an elevated temperature from the gas discharge nozzle deployed adjacent to the spinning nozzle, thereby generating a flow of ultra-fine elastic fibers, and collecting them to sheet form by an advancing conveyer net with an suction exhaust gas device at the portion where the fibers flow blows.

The distance between the spinning nozzle and the conveyer net is preferable to be settled as from 10 to 30 cm in order to maintain the favorable sheet form, comfortable tactile, flexibility, elasticity and gas-permeability of the non-woven fabric made from polyurethane ultra-fine elastic fiber. When the distance exceeds 30 cm, it becomes difficult to maintain the favorable sheet form. Further, when the distance is shorter than 10 cm, the adhesion between the single fibers themselves becomes too exaggerating to lose the comfortable tactile of the non-woven fabric.

Additionally, it is possible to use additives such as optical stabilizer, pigment and others as far as it does not give any influence on the favorable physical properties of the non-woven fabric made from polyurethane ultra-fine elastic fiber.

Because the non-woven fabric made from polyurethane ultra-fine elastic fiber according to the present invention has favorable warm tactile, flexibility, elasticity and moisture permeable waterproof property, it may be used in various usages utilizing these merits. It may be used alone or combined with another non-woven fabric, textile or knits. Specifically, it may be used for materials for clothing such as sports casual wears, raincoats, wind breakers, foundations, and artificial leathers for clothing, or medical sanitary materials such as means for medical operation, substrate cloth for poultice, substrate for bandages, diaper covers and so on.

[Examples]

In the following, the present invention will be described in more detail with reference to working examples, which however, shall never limit the present invention thereto. The measurements about values of the various physical properties were conducted in accordance with the following methods and conditions.

Strength and degree of elongation:

It was measured under the drawing rate of 30 cm/minute with the

use of a specimen having a width of 2.5 cm and a length of 10 cm.

Recovery ratio of elongation:

It was calculated after obtaining a residual elongation ratio drawing 100 % under the drawing rate of 10 cm/minute about a specimen having a width of 2.5 cm and a length of 10 cm and soon recovering to the original size under the same rate.

Bending resistance:

It was measured with the use of a test piece having a width of 2.5 cm by a 45 degrees cantilever method in accordance with JIS-L1096.

Water resistant pressure:

It was measured in accordance with JIS-1092B method.

Moisture permeability:

It was measured in accordance with JIS-Z-0208.

Tactile:

It was determined by sensually evaluating the tactile by a human hand about a specimen having a width of 20 cm and a length of 20 cm.

Example 1

Polyurethane having 4.0 % by weight of nitrogen atom was obtained by melt polymerization of the polyester diol having mean molecular weight of 1000 consisting of 3-methyl-1,5-pentane diol and adipic acid, 1,4 butane diol and 4,4-diphenyl-methane diisocyanate.

A meltblown method was conducted with the use of a meltblown apparatus described in Japanese Unexamined Laid Open Patent Application No. SHOU 49-48921, etc., by arranging the spinning nozzles having diameter of 0.3 mm in a row with 1 mm pitch, and disposing slit-shaped gas discharge slots with the thickness of 0.25 mm on both sides of the row, discharging the foregoing polyurethane with the rate of 0.20 g/minute per spinning nozzle at the melting temperature of 250 °C, and jetting the heated air with the temperature of 250 °C from the slit-shaped gas discharge slots at the pressure of 1.5 g/cm² gauge. Then, a non-woven fabric made from polyurethane ultra-fine elastic fiber was obtained by collecting the jetted fibers flow over a belt conveyor advancing at the position 23 cm lower under the spinning nozzles.

The polyurethane non-woven fabric had a favorable sheet form after mere collecting. The observation of this non-woven fabric under a scanning electron microscope with enlarging 500 magnifications showed that the

average diameter was 8 μm . Although bundling between the fibers was recognized, favorable tactile, flexibility, elastic property, and moisture permeable waterproof property were verified along with the physical properties of the non-woven fiber as the following:

- Mass per unit area: 57 (g/m^2)
- Strength: 1.5 ($\text{kg}/2.5\text{cm}$)
- Degree of elongation: 290 (%)
- Tactile: fibrous and warm
- Recovery ratio of elongation after 100 % elongation: 91 (%)
- Bending resistance: 31 (mm)
- Water resistant pressure: 400 (mmH_2O)
- Moisture permeability: 9050 ($\text{g}/\text{m}^2/24\text{hrs}$)

A sports casual shirt obtained after combining in contact with a fabric having elasticity in both longitudinal and lateral direction by making this non-woven fabric as flesh side had favorable tactile as well as excellent elasticity and moisture permeable waterproof property.

The durability of the non-woven fabric was evaluated comparing with the strength or the retention of the degree of elongation before and after soaking it in warm water having the temperature of 90 $^{\circ}\text{C}$ for five days and verified to be extremely superior having the retention of 90 % or greater.

Comparative Example 1

Comparative Example 1 was conducted with almost the same conditions as Example 1 with the use of the same meltblown apparatus except that discharging the foregoing polyurethane with the rate of 0.5 g/minute per spinning nozzle, and jetting the heated air from the slit-shaped gas discharge slots at the pressure of 0.9 g/cm^2 gauge.

The polyurethane non-woven fabric obtained with this condition was formed by fibers of having the average fiber diameter of 14 μm and bundling between the fibers was recognized.

The non-woven fabric had a coarse and hard texture, inferior waterproof property, and poor practical use value with physical properties as the following:

- Mass per unit area: 110 (g/m^2)
- Strength: 0.7 ($\text{kg}/2.5\text{cm}$)
- Degree of elongation: 300 (%)

- Tactile: fibrous but coarse and hard
- Recovery ratio of elongation after 100 % elongation: 92 (%)
- Bending resistance: 65 (mm)
- Water resistant pressure: 80 (mmH₂O)
- Moisture permeability: 10200 (g/m²/24hrs)

Comparative Example 2

A non-woven fabric made from polyurethane ultra-fine elastic fiber was obtained by conducting the meltblown method with almost the same apparatus and conditions as Example 1 except that the polyurethane was obtained by melt polymerization of the polyester diol having mean molecular weight of 500 consisting of 3-methyl-1,5-pentane diol and adipic acid, 1,4 butane diol and 4,4-diphenyl-methane diisocyanate.

Although the mean fiber diameter of this non-woven fabric was 8 μ m, this non-woven fabric had an inferior elasticity with the physical properties as the following:

- Mass per unit area: 58 (g/m²)
- Strength: 1.1 (kg/2.5cm)
- Degree of elongation: 130 (%)
- Tactile: fibrous and warm
- Recovery ratio of elongation after 100 % elongation: 85 (%)
- Bending resistance: 30 (mm)
- Water resistant pressure: 420 (mmH₂O)
- Moisture permeability: 7500 (g/m²/24hrs)

The durability having main concern on hydrolysis resistance of the non-woven fabric was evaluated comparing with the strength or the retention of the degree of elongation before and after soaking it in warm water having the temperature of 90 °C for five days and verified to be inferior having the retention of only 44 % or more.

Comparative Example 3

The meltblown method was tried with almost the same apparatus and conditions as Example 1 except that the polyurethane was obtained by melt polymerization of the polyester diol having mean molecular weight of 5000 consisting of 3-methyl-1,5-pentane diol and adipic acid, 1,4 butane diol and 4,4-diphenyl-methane diisocyanate. However, any non-woven fabric

made from polyurethane ultra-fine elastic fiber was unable to be obtained in this case, because breakings of the polyurethane discharge flow occurred adjacent around the spinning nozzles obstructed the sufficient thinning or ultra-thinning of the polyurethane fibers.

Comparative Example 4

The meltblown method was tried with almost the same apparatus and conditions as Example 1 except that the polyurethane was obtained by melt polymerization with the use of poly tetramethylene ether glycol having mean molecular weight of 1100 instead of polyester poly diol.

However, it was difficult to conduct stable meltblown method in this case, because the thermal decomposition of the polyurethane under melt situation was exaggerating.

The resultant fabric obtained by collecting the fibers in sheet form without stability had poor mechanical properties such as elasticity or so and was inappropriate for practical use.